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EP-A- 0 221 400
ABSTRACT BULLETIN OF THE INSTITUTE OF
PAPER CHEMISTRY, vol. 57, no. 10, April 1987,
page 1469, abstract 13393, Appleton, Wiscon-
sin, US
ABSTRACT BULLETIN OF THE INSTITUTE OF
PAPER CHEMISTRY, vol. 58, no. 1, July 1987,
page 137, abstract no. 1067, Appleton, Wiscon-
sin, US
ABSTRACT BULLETIN OF THE INSTITUTE OF
PAPER CHEMISTRY, vol. 53, no. 10, April 1983,
page 1190, abstract no. 1190, Appleton, Wis-
consin, US
ABSTRACT BULLETIN OF THE INSTITUTE OF
PAPER CHEMISTRY, vol. 55, no. 5, November
1984, page 631, abstract no. 5991, Appleton,
Wisconsin, US

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Description

The present invention relates to a papermaking method of preparing a paper having a reinforced strength, where a latex emulsion having a cationic-anionic amphoteric functional group and having an amphoteric ion-complex structure is added to the paper stock.

As the polymer latex (or emulsion) usable as an additive to the paper stock in papermaking, an anionic substance is generally known. In the case, it is necessary that the polymer latex is employed along with aluminium sulfate or a cationic water-soluble polymer whereby the latex grains are coagulated and coarsened to be well fixed to the paper stock.

JP-A-61-261302 mentions cationic polymer latexes.

As opposed to this, the applicant's own JP-A-1-146907 (published 8th June 1989) mentions a polymer latex of composite structure having amphoteric ions as distributed highly densely on the surfaces of the emulsion grains.

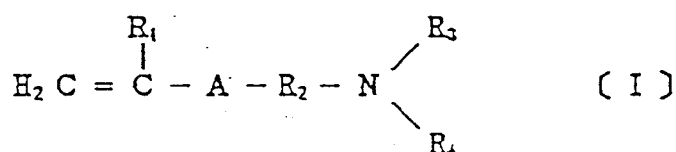
The polymer latex to be employed as an additive to a paper stock is required to have higher fixability and also have higher bindability and adhesiveness to fibers or a filler, because of the economic price race.

The latex to be employed in the method of the present invention may have amphoteric ions at the same time and display a cationic property in average. Accordingly, it has not only a function of adsorbing to fibers or a filler but also an interaction between the latex grains themselves. Therefore, it may have an excellent self-fixability even though it is not combined with an additional fixing agent such as aluminium sulfate or a cationic water-soluble polymer.

The paper to be prepared by preferred embodiments of the papermaking method of the present invention has noticeably improved bursting-resistance, tensile strength, bending-resistance and tear strength. In particular, when a small amount of the polymer latex of the invention is added to a paper stock for preparing a high filler-containing paper which often has a lowered strength, the paper obtained may have an improved paper strength.

In addition, the polymer latex of the present invention is also effective for noticeably improving the inter-layer-peeling strength in a laminate-structural paper. Moreover, preferred embodiments provide a papermaking method of preparing excellent papers with good hand, high gas-permeability and sufficient adhesiveness, and the producibility of the papermaking method is high.

The present invention provides a method of preparing a paper having a reinforced strength wherein a polymer latex is added to a paper stock in an amount of from 2.5 to 30 % by weight, which is characterized in that the polymer latex is one prepared by neutralizing a seed polymer with an acid or a salt or by quaternizing it with a quaternizing agent, the surfaces of the emulsion grains being thereby highly densely cationated, where the seed polymer is formed by adding a monomer as represented by the following formula (I) or a mixture of the monomer (I) and copolymerizable ethylenic unsaturated monomer(s) (II) to a seed latex of a carboxyl-modified synthetic rubber latex or synthetic resin emulsion and polymerizing them:

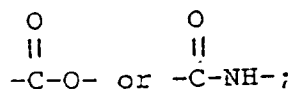


in which R_1 represents H or CH_3 ;

R_2 represents an alkylene group having from 2 to 5 carbon atoms;

R_3 and R_4 each represent H or an alkyl group having from 1 to 5 carbon atoms;

A represents

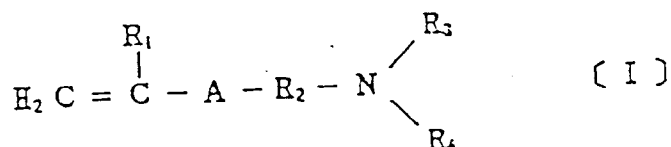


and

R_1 , R_3 and R_4 are so selected that the monomer is hardly soluble or insoluble in water.

Desirably, the amount of the monomer of the formula (I) as added corresponds to the colloid-equivalent value (absolute value) of the carboxyl-modified latex or more. In a preferred form, the invention provides a

method of preparing a paper having a reinforced strength wherein a polymer latex is added to a paper stock in an amount of from 2.5 to 30 % by weight, which is characterized in that the polymer latex is a highly densely cationated polymer emulsion as prepared by neutralizing a seed polymer with an acid or a salt or by quaternizing it with a quaternizing agent whereby the surfaces of the emulsion grains are highly densely cationated, where the seed polymer is one obtained by polymerizing a seed latex of a carboxyl-modified synthetic rubber latex or synthetic resin emulsion as previously neutralized to a pH value of 6 or more and a monomer as represented by the following formula (I) or a mixture of the monomer (I) and copolymerizable ethylenic unsaturated monomer(s) (II) as added to the neutralized seed latex in such proportion that the amount of the monomer (I) corresponds to at least not less than the colloid-equivalent value (absolute value) of the seed latex, in the presence of a radical polymerization initiator:

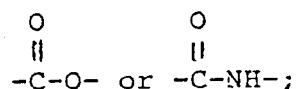


in which R_1 represents H or CH_3 ;

R_2 represents an alkylene group having from 2 to 5 carbon atoms;

R_3 and R_4 each represent H or an alkyl group having from 1 to 5 carbon atoms;

A represents



and

R_1 , R_2 and R_4 are so selected that the monomer is hardly soluble or in soluble in water.

DETAILED EXPLANATION OF THE INVENTION

The present invention is characterized by the employment of a high polymer latex having an amphoteric ion-composite structure. Such functional latex is prepared by seed polymerization of a carboxyl-modified anionic seed latex and other monomers followed by neutralisation with an acid or a salt, or by quaternisation of the resulting seed polymer. The thus prepared functional latex has cationic groups as distributed highly densely on the surfaces of the latex grains, and it has amphoteric ions and is cationically charged in average.

As being prepared by seed polymerization, the functional latex of the present invention has a composite-layered structure and it displays the characteristics of the synthetic rubber or resin used as the seed latex.

Since the functional latex has amphoteric ions, it may well be adsorbed to oppositely charged fine fibers or filler in water during the papermaking process. Additionally, as the latex grains themselves have an ionic interaction therebetween, the fixability and the fused strength of the latex grains are strong during the papermaking and drying steps. Accordingly, the adhesiveness of the latex in the paper prepared is high and the paper strength thereof is improved.

The papermaking procedure is effected under an acidic or neutral condition. For example, it is stable at pH of from 4 to 9.

The papermaking process of the present invention does not require any secondary treatment such as impregnation. Further, it is free from a drawback of binder migration in drying. Accordingly, the excellent producibility of the present invention can be attained only by the primary treatment of adding the particular polymer latex to the paper stock.

The method of preparing the polymer latex which is employed in the papermaking process of the present invention is described in the forementioned JP-A-1-146907. The content will be explained hereunder.

As the synthetic rubber latex or synthetic resin emulsion for use in the present invention, anyone known in the technical field can be employed.

As examples of the synthetic rubber latex usable in the present invention, there are mentioned carboxyl-modified latexes of styrene-butadiene rubber (SBR), methyl methacrylate-butadiene rubber (MBR), acrylonitril-butadiene rubber (NBR) or a rubber comprising the said rubber and other monomer component(s) (α), as

well as chloroprene rubber (CR) or isoprene rubber (IR). As examples of the synthetic resin emulsion also usable in the present invention, there are mentioned carboxyl-modified emulsions of polymers or copolymers of acrylates, vinyl acetate, vinyl chloride or styrenes, as well as ethylene-vinyl acetate copolymers or ethylene-vinyl chloride copolymers.

The particular monomers for use in the present invention include the monomers represented by the general formula (I) and ethylenic unsaturated monomers (II) which are copolymerizable with the monomers (I).

As examples of the monomers of the formula (I), there are mentioned diethylaminoethyl acrylate, diethylaminoethyl methacrylate, dipropylaminoethyl acrylate, dipropylaminoethyl methacrylate, dibutylaminoethyl methacrylate, t-butylaminoethyl (meth)acrylate, diethylaminopropyl-methacrylamide, dipropylaminopropyl-methacrylamide, dipropylaminopropyl-acrylamide, dibutylaminopropyl-methacrylamide and dibutylaminopropyl-acrylamide.

Other ethylenic unsaturated monomers (II) which are copolymerizable with the monomers (I) include, for example, hydrophobic monomers such as acrylates, methacrylates, acrylonitriles, styrenes or vinyl acetate, as well as crosslinking monomers such as N,N'-methylenebisacrylamide, diallyl phthalate, divinyl-benzene and (poly)ethylene glycol di (meth)acrylates.

The amounts of the above-mentioned raw materials to be employed in accordance with the present invention are as mentioned below.

The proportion monomer of the formula (I) to the seed latex is approximately from 5 to 50 % by weight, preferably from 10 to 30 % by weight.

In general, ordinary carboxyl-modified latexes have a colloid-equivalent value of from -0.2 to -0.1 meq/g. Accordingly, if the proportion of the monomer of the formula (I) to be employed in the present invention is less than 5 % by weight, a stable cationic latex could not be obtained as the amount of the cationic groups is too small. On the contrary, however, if it is more than 50 % by weight, the cationic groups would be economically disadvantageously excessive.

The colloid-equivalent value is obtained by the method mentioned below.

95 ml of a distilled water is put in a beaker, 5 ml of a 1000-ppm solution of a sample is added thereto, the content is adjusted to have a pH value of 4.0 with 1 %-HCl, and the whole is stirred for about one minute. Next, two or three drops of a solution of Toluidine Blue indicator are added to the resulting blend, which is then titrated with N/400 PVSK (potassium polyvinyl sulphate). The titration speed is 2 ml/min. The time when the color of the test water changes from blue to red and the changed color is kept as it is for 10 seconds or more is the final point. The colloid-equivalent value is calculated from the following formula:

$$\text{Colloid - Equivalent Value (meq/g)} = \frac{(\text{Amount of Sample Titration} - \text{Amount of Blank Titration}) \times F}{2}$$

In the formula, F indicates a factor.

The amount of the monomer (II) to be used in the invention can be determined in accordance with the glass transition point or other physical properties of the intended latex. In general, it may be from 0 to about 40 % by weight to the monomer (I). The polymerization is effected by seed polymerization, where the pH value of the polymerization system is made to be 6 or more, after the seed latex is diluted or is not diluted with water, and the above-mentioned monomers are added to the system and stirred at a temperature of 20 to 80°C in the presence of a radical polymerization initiator for seed-polymerization.

If the pH value of the polymerization system is less than 6, the system would gel when the monomers are added thereto or when the monomers are polymerized and, as a result, a stable emulsion could not be obtained. Although the polymerization temperature is not specifically defined under normal pressure, it falls practically within the range of from 20 to 80°C, preferably from 30 to 60°C.

In the polymerization step, an additional surfactant would not be specifically necessary but may be added to the polymerization system if the content is insufficient.

The radical polymerization initiator for use in the present invention may be anyone employable in conventional emulsion polymerization.

For instance, there are mentioned inorganic peroxides such as ammonium persulfate, potassium persulfate or hydrogen peroxide; aliphatic azo compounds such as azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(2-amidinopropane)hydrochloride or azobis(N,N'-dimethyleneisobutylamide)hydrochloride; benzoyl peroxide; hydroperoxides such as t-butylhydroperoxide, diisopropylbenzene-hydroperoxide or cumene-hydroperoxide; and redoxes comprising a combination of the above-mentioned peroxide and a reducing agent such as ascorbic acids, polyvalent metal salts, acidic sodium sulfite or sodium formaldehyde-sulfoxylate.

The amount of the polymerization initiator to be used in the polymerization process is approximately from 1.0 to 5.0 % by weight of the monomers. The polymerization may be conducted by either a batch-wise system or a continuous system.

Next, the resulting polymer is neutralized with an acid or a salt or is quaternary-ammoniated with an or-

dinary quaternating agent, whereby a cationic polymer emulsion where the cationic groups are distributed highly densely on the surfaces of the latex grains is obtained.

For cationation, an acid, salt or quaternizing agent is added to the seed polymer in an amount equivalent to the monomer (I), with stirring at room temperature, whereupon neutralization finishes instantly and quaternization finishes generally in approximately from 5 to 30 minutes.

The acid employable for the process includes inorganic acids such as hydrochloric acid or sulfuric acid and organic acids such as acetic acid, adipic acid, citric acid or formic acid; the salt includes acidic salts such as sodium hydrogensulfate or sodium dihydrogenphosphate; and the quaternizing agent include alkyl halides such as methyl chloride, ethyl chloride, methyl bromide or methyl iodide and other ordinary alkylating agents such as dimethyl sulfate or diethyl sulfate.

The following examples are intended to illustrate the process of a polymer latex of the present invention in more detail.

15 Preparation EXAMPLE 1:

701.3 g of a carboxyl-modified SBR latex (pH 8.3; solid content 48 %; anion colloid-equivalent value -0.18 meq/g), 0.4 g of N,N'-methylenebisacrylamide and 159.7 g of water were put in a flask equipped with a stirrer. With fully stirring, 37.5 g of diethylaminoethyl methacrylate (cation colloid-equivalent value of 0.51 meq/g, as quaternated dimethyl sulfate) was dropwise added thereto through a dropping funnel and thereafter the content in the flask was allowed to stand as it was for one hour with blowing N₂ gas thereto. Afterwards, 80 g of 1 % aqueous potassium persulfate solution was added to the reaction mixture, which was then heated up to 50°C for polymerization. The polymerization finished in about 2 hours.

30 g of dimethyl-sulphuric acid which is equivalent to the amount of the diethylaminoethyl methacrylate was dropwise added to the polymer latex with stirring for quaternation to obtain an amphoteric polymer latex.

Preparation EXAMPLE 2:

The same operation as in Example 1 was repeated, except that N,N'-methylenebisacrylamide was not added, and a stable amphoteric polymer latex was obtained.

Preparation EXAMPLE 3:

530 g of a carboxyl-modified MBR latex (pH 8.8; solid content 45 %; anion colloid-equivalent value -0.20 meq/g) and 55 g of water were put in a flask equipped with a stirrer. With well stirring, 20 g of methyl methacrylate and 40 g of diethylaminoethyl methacrylate were dropwise added thereto through a dropping funnel and thereafter the content was allowed to stand as it was for one hour with blowing N₂ gas thereto. Afterwards, 120 g of 1 % potassium persulfate was added to the reaction mixture, which was then heated up to 40°C for polymerization. The polymerization finished in about 3 hours.

32 g of dimethyl-sulfuric acid which is equivalent to the amount of the diethylaminoethyl methacrylate was dropwise added to the polymer latex with stirring for quaternation to obtain an amphoteric polymer latex.

Preparation EXAMPLE 4:

The same operation as in Example 3 was repeated, except that the methyl methacrylate was replaced by vinyl acetate, and a stable amphoteric polymer latex was obtained.

Preparation EXAMPLE 5:

The same operation as in Example 1 was repeated, except that the diethylaminoethyl methacrylate was replaced by t-butylaminoethyl methacrylate, and a stable amphoteric polymer latex was obtained.

Next, the method of adding the polymer latex to a paper stock to be used for the papermaking method of the present invention will be mentioned below.

The polymer latex is effectively added to the paper stock (pulp and filler) in an amount of approximately from 2.5 to 30 % by weight as the solid content. It may be more than 30 % by weight, but the fixability would lower and the effect would thereby lower.

The amount of the polymer latex to be added to the paper stock is selected in accordance with the paper-making condition and the characteristics of the paper products to be prepared. It is preferred to previously determine the amount by a preliminary test where the range for sufficient fixation is measured, for example, by

the use of a dynamic drainage jar.

The polymer latex may fix to the paper stock almost completely in an amount of up to 20 % by weight. It is preferred that the polymer latex is previously diluted with water to 1/10 or less prior to being added to the paper stock.

In the papermaking method of the present invention, a fixing agent such as aluminium sulfate is not specifically necessary but is preferably employed along with a retention-improving agent for the purpose of improving the retention of fine fibers and fillers in the method. The position of adding the agent is preferably before the machine chest or run pump.

Where a retention-improving agent is employed, it is preferably added at the position before and/or after the screen or near the head box.

EXAMPLE 1:

A fixation test was effected, where the latex mentioned below was added to the paper stock mentioned below. The conditions were as follows:

(1) Pulp Used: 1 % LBKP Slurry (degree of beating: 400 ml C.S.F.)

(2) The amphoteric latex prepared in preparation Example 1 was used as the polymer latex.

(3) Test Method: The pulp slurry was put in a dynamic drainage jar and a determined amount of the polymer latex was added thereto. Then the whole was stirred at 800 rpm for 230 seconds and filtered through a screen having sieve openings : 0.105 mm (150-mesh screen). The colloid-equivalent value of the resulting filtrate was obtained on the basis of the definition mentioned above, and the fixation percentage was calculated out therefrom.

(4) The results obtained are shown in Table 1 below.

EXAMPLE 2:

A paper-strength improving test was effected, using a paper made from a polymer latex-added paper stock. The papermaking conditions were as follows:

(1) Pulp Used: NBKP (degree of beating: 400 ml/700 ml C.S.F. LBKP (degree of beating: 400 ml/700 ml C.S.F.

(2) The product prepared in preparation Example 1 was used as the polymer latex. The amount added was 0, 5 or 10 parts by dry weight to the pulp.

(3) Weight of Paper(Base weight): 60 g/m²

(4) Papermaking Machine Used: TAPPI Sheet Machine

(5) Press: 5 kg/cm² x 15 min.

(6) Drying: 120°C x 2 min in drum drier.

(7) The relative breaking strength was measured. The results obtained are shown in Table 2 below.

EXAMPLE 3:

A paper made from a polymer latex-added paper stock having a high filler content was tested under the conditions mentioned below. As the polymer latex, the product produced in preparation Example 1 was used.

(1) Raw Material:

Pulp : NBKP (400 ml CSF)

Pigment : Aluminium Hydroxide

Blend Ratio : NBKP/Aluminium Hydroxide of 15/85 (by weight)

Amount of Latex Added : 0 to 10 % by dry weight to pulp

Accurac MG1024 (filler retention-improving agent, trade name of Mitsui-Cyanamid, Ltd.) (ACCU-RAC is a registered trade mark) :

0.1 % by dry weight to pulp

Synthetic Formation Aid (polyethylene oxide):

0.1 % by dry weight to pulp

(2) Papermaking Conditions:

Base Weight : 200 g/m²

Press : 3 kg/cm² x 15 min

Drying : 120°C x 2 min in drum drier

130°C x 5 min in hot-air drier

Order of Addition : Pulp → Latex → Accurac MG1024 → Synthetic Formation Aid → Papermaking

(3) The test results are shown in Table 3 below.

In accordance with the papermaking method of the present invention, a paper having a noticeably improved paper-strength is prepared. This invention may be used in the fields mentioned below.

Wet non-woven fabric, inorganic fiber paper, high filler paper, ceramic paper, printing paper for poster, map or label, polishing paper, masking tape, adhesive tape base, oil-proof wrapping paper, wall paper base, imitation leather paper base, gasket paper, bottom or core for shoe, packing, floor mat base, etc.

Table 1

Latex Added (wt%/Pulp)	Fixation (%)
2.5	100
5	100
10	100
15	100
20	100
30	96

Table 2

Pulp Used	Degree of Beating (mLCSF)	Latex Added (wt%/Pulp)	Relative Breaking Strength
NBKP	400	0	4.6
		5	5.9
		10	6.4
NBKP	700	0	1.0
		5	3.0
		10	4.4
LBKP	400	0	2.8
		5	3.5
		10	4.3
LBKP	700	0	0.1
		5	0.9
		10	1.5

Table 3

No	Raw Material (wt%)			Base Weight (g/m ²)	Al(OH) ₃ in Paper (%)	Bursting Strength (kg/cm ²)	Relative Breaking Strength
	Latex	Accupac [®] MG 1024	Formation Aid				
A	0	0.1	0.1	154	82	0.11	0.07
B	2.5	0.1	0.1	138	78	0.80	0.43
C	5	0.1	0.1	131	77	0.71	0.54
D	10	0.1	0.1	125	75	0.88	0.70
E	10	—	0.1	67	51	1.54	2.30
F	10	—	—	70	51	1.62	2.31

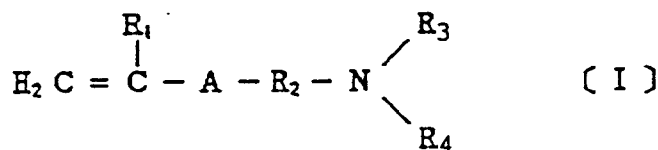
Remarks: As to NO. E, F, Retention Aid is not added, so retention of Al(OH)₃ in paper is small.

Furthermore, apparent Strength is high on account of increased fiber in paper.

Claims

1. A method of preparing a paper having a reinforced strength wherein a polymer latex is added to a paper stock in an amount of from 2.5 to 30 % by weight, which is characterized in that the polymer latex is one prepared by neutralizing a seed polymer with an acid or a salt or by quaternizing it with a quaternizing agent, the surfaces of the emulsion grains being thereby highly densely cationated, where the seed polymer is formed by adding a monomer as represented by the following formula (I) or a mixture of the mono-

mer (I) and copolymerizable ethylenic unsaturated monomer(s) (II) to a seed latex of a carboxyl-modified synthetic rubber latex or synthetic resin emulsion and polymerizing them:

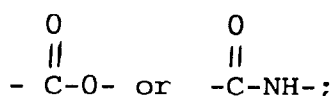


in which R_1 represents H or CH_3 ;

R_2 represents an alkylene group having from 2 to 5 carbon atoms;

R_3 and R_4 each represent H or an alkyl group having from 1 to 5 carbon atoms;

A represents



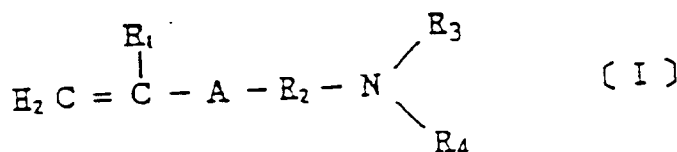
and

R_1 , R_3 and R_4 are so selected that the monomer is hardly soluble or insoluble in water.

2. The method as claimed in claim 1, in which the amount of the monomer of the formula (I) as added corresponds to the colloid-equivalent value (absolute value) of the carboxyl-modified latex or more.
3. A method as claimed in claim 1 wherein in the process of forming the seed polymer, the seed latex is first neutralized to a pH value of 6 or more; and the monomer (I) or mixture of monomers (I) and (II) is/are added to the neutralized seed latex in such proportion that the amount of the monomer (I) corresponds to at least the colloid-equivalent value (absolute value) of the seed latex; and said polymerisation is effected in the presence of a radical polymerisation initiator.

Patentansprüche

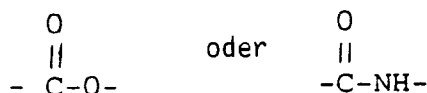
1. Verfahren zur Herstellung eines Papiers mit verstärkter Festigkeit, bei dem ein Polymerlatex einem Papierstoff in einer Menge von 2,5 bis 30 Gew.-% hinzugefügt wird, dadurch gekennzeichnet, daß der Polymerlatex einer ist, der durch Neutralisieren eines körnerbildenden Polymers mit einer Säure oder einem Salz oder durch Quaternisieren mit einem Quaternisierungsmittel einem Salz oder durch Quaternisieren mit einem Quaternisierungsmittel hergestellt wird, wobei die Oberflächen der Emulsionskörner dadurch hochdicht kationisiert werden, wobei das körnerbildende Polymer gebildet wird, indem ein durch die folgende Formel (I) dargestelltes Monomer oder eine Mischung aus dem Monomer (I) und copolymerisierbaren/-em äthylenischem/-en ungesättigtem/-en Monomer(en) (II) einem körnerbildenden Latex aus carboxylmodifiziertem Kunstgummilatem oder Kunstharzemulsion hinzugefügt und sie polymerisiert werden:



worin R_1 H oder CH_3 darstellt;

R_2 eine Alkylengruppe darstellt, die von 2 bis 5 C-Atome aufweist;

R_3 und R_4 jeweils H oder eine Alkylgruppe mit von 1 bis 5 C-Atomen darstellen; A



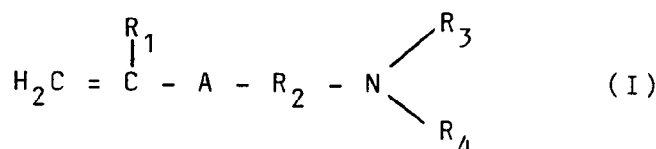
darstellt; und

R₁, R₃ und R₄ so ausgewählt sind, daß das Monomer in Wasser kaum löslich oder unlöslich ist.

2. Verfahren nach Anspruch 1, bei dem die Menge des Monomers der Formel (I) wie hinzugefügt dem Kolloidäquivalentwert (absoluten Wert) des carboxylmodifizierten Latex oder mehr entspricht.
3. Verfahren nach Anspruch 1, worin beim Verfahren zum Bilden des körnerbildenden Polymers der körnerbildende Latex zuerst auf einen pH-Wert von 6 oder mehr neutralisiert wird; und das Monomer (I) oder die Mischung aus Monomeren (I) und (II) dem neutralisierten körnerbildenden Latex in einem solchen Anteil hinzugefügt wird/werden, daß die Menge des Monomers (I) zumindest dem Kolloidäquivalentwert (absoluten Wert) des körnerbildenden Latex entspricht; und die genannte Polymerisation in Gegenwart eines Radikalpolymerisationsinitiators durchgeführt wird.

Revendications

1. Méthode de préparation d'un papier ayant une meilleure résistance, où on ajoute un latex de polymère à un produit de papier en une quantité de 2,5 à 30% en poids, qui est caractérisée en ce que le latex de polymère est préparé en neutralisant un polymère d'ensemencement avec un acide ou un sel ou en le quaternisant avec un agent quaternisant, les surfaces des grains de l'émulsion étant ainsi très densément cationés, où le polymère d'ensemencement est formé en ajoutant un monomère représenté par la formule (I) qui suit ou un mélange du monomère (I) et d'un ou plusieurs monomères copolymérisables à insaturation éthylénique (II) à un latex d'ensemencement d'un latex d'un caoutchouc synthétique modifié par un carboxyle ou d'une émulsion de résine synthétique et en polymérisant :

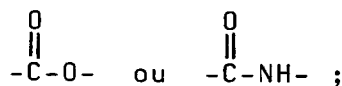


où R₁ représente H ou CH₃ ;

R₂ représente un groupe alkylène ayant 2 à 5 atomes de carbone ;

chacun de R₃ et R₄ représente H ou un groupe alkyle ayant 1 à 5 atomes de carbone ;

A représente



et

R₁, R₃ et R₄ sont choisis de façon que le monomère soit à peine soluble ou insoluble dans l'eau.

2. Méthode selon la revendication 1, où la quantité du monomère de la formule (I), comme on l'ajoute, correspond à la valeur équivalente du colloïde (valeur absolue) du latex modifié par un carboxyle ou plus.
3. Méthode selon la revendication 1 où, dans le procédé de formation du polymère d'ensemencement, le latex d'ensemencement est d'abord neutralisé à une valeur de pH de 6 ou plus ; et ensuite le monomère (I) ou le mélange des monomères (I) et (II) est ou sont ajoutés au latex neutralisé d'ensemencement à une proportion telle que la quantité du monomère (I) corresponde au moins à la valeur d'équivalent de colloïde (valeur absolue) du latex d'ensemencement ; et ladite polymérisation est effectuée en présence d'un initiateur de polymérisation radicalaire.